Chemo-catalytic synthesis of biobased higher alcohols

Xi, Xiaoying

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Summary

Higher alcohols have attracted considerable interest owing to their broad range of applications. For application as a fuel in combustion engines, issues related to the use of ethanol as a fuel (additive) may be alleviated by using C3+ alcohols. Higher alcohols derived from biomass with a high C3+ alcohol content are thus highly promising biofuels. In addition, higher alcohols are also in demand in the chemical industry, and are precursors for olefins and the preparation of plasticizers and detergents. Nowadays, higher alcohols are mainly manufactured through either fermentation technology with high energy demand, or the hydration of alkenes with very low single-pass conversion and high dependence on unsustainable petroleum oil. Therefore, new catalytic technology with sustainability advantages needs to be developed in order to meet the increasing demand for higher alcohols. This PhD project focused on the design of enhanced heterogeneous catalysts for biobased higher alcohol synthesis from syngas conversion (Chapter 2 and 3), CO_2 hydrogenation (Chapter 4) and the Guerbet coupling of bioethanol (Chapter 5).

Recent developments of higher alcohol synthesis from CO hydrogenation, CO_2 hydrogenation and the Guerbet coupling of ethanol at the molecular level (catalyst systems and reaction mechanisms), together with the state-of-the-art catalyst performance are provided in **Chapter 1**. Catalytic sites active for the formation of adsorbed CH_x* and $C(H_x)O$* species in close proximity are required for both CO and CO_2 hydrogenation to higher alcohols. For the Guerbet coupling of ethanol, the employed catalysts require a proper balance between basic/acid sites and dehydrogenation/hydrogenation activity. Catalytic systems featuring high activity, selectivity and stability are required for future large-scale processes.

In **Chapter 2**, experimental studies are reported on the use of K promoted MoS_2 (K-MoS_2) catalysts for CO hydrogenation to higher alcohols with enhanced C3+ alcohol contents. The structure of the K-MoS_2 catalysts was tailored by using a thermal treatment involving a mixture of amorphous $MoS_{3.7}$ and K_2CO_3. By this approach, a multilayer structure with MoS_2 and K-MoS_2 mixed phases are formed. This multilayer structure with reduced exposure of rim sites and intimate contact between the MoS_2 and $KMoS_2$ phase fosters carbon chain growth and C3+ alcohol production. Remarkably, the alcohol distribution differs from the expected ASF distribution as a result of enhanced CO insertion and CH_x β-addition. By tailoring the K/Mo

ratio, the formation of alcohols and C3+ alcohols in particular under appropriate reaction temperature was optimized. The findings were rationalized by considering the relative ratio of the $KMoS_2$ and MoS_2 phases, which was shown to be an important parameter and tunable by the K/Mo ratio. A higher alcohol selectivity of 29.1–32.7% and C3+ alcohol yield of 3.6–5.1%, as well as good stability were obtained by catalyst design and optimizing the reaction conditions.

On the basis of the results obtained in Chapter 2, the addition of Co to the K-MoS_2 catalysts was investigated to further enhance C3+ alcohol yields and the results are provided in **Chapter 3**. A series of K-Co-MoS_x catalyst with different Co contents and a fixed K content were prepared to investigate the effect of Co promotion on product selectivity and particularly C3+ alcohol formation from syngas. The preparation of the Co-MoS_x samples through sulfurization of cobalt-molybdenum oxide precursors leads to among others the formation of Co-Mo-S and CoS_2 phases, the actual amounts being dependent on the Co amount in the catalyst formulation. The catalyst giving the best performance contains the highest amounts of Co-Mo-S and Co_9S_8 phases, implying that these are preferred for higher alcohol synthesis. It is speculated that close contact between a K modified Co_9S_8 phase and a Co promoted Mo-S phases is beneficial for higher alcohol synthesis due to facile transfer of adsorbed CH_x* species (and higher analogs) on the Co_9S_8 phase to oxygenated species on the Co promoted Mo-S phase to give branched higher alcohols and transfer of adsorbed $CH_3CH_2CH_2$* on the Co_9S_8 phase to adsorbed CO on the K-(Co)MoS phase to give linear alcohols. Reaction conditions (T, P, GHSV and H_2/CO ratio) were varied to study the effect on catalytic performance and statistical models with high significance were developed. Highest C3+ alcohol yields of 7.3–9.2% and selectivities between 31.0–37.6% were obtained at a temperature of 380 °C, a pressure of 11.7 MPa, a GHSV of 13500–27000 mL g^{-1} h^{-1} and H_2/CO ratio of 1 over the optimized K-Co-MoS_x-0.13 catalyst. These results are the highest reported in the literature so far, and indicate the potential of such catalysts for further scale up studies.

The synthesis of higher alcohols from CO_2 hydrogenation is discussed in **Chapter 4**. We have prepared a series of FeIn/Ce-ZrO_2 catalysts with different Fe/(Fe+In) molar ratios and shown that such bimetallic FeIn catalyst when promoted with K are active and stable catalyst for the hydrogenation of CO_2 into higher alcohols (maximum yield of 8.5%), after activation under a CO atmosphere. Catalyst characterization and product selectivity data reveal that K promotion

suppresses hydrogenation activity to smaller molecules and as such favors higher alcohol formation. A mechanism is proposed where efficient transfer of CH_x* intermediates on iron species (likely carbides) to adsorbed H_xCO* on In results in the formation of higher alcohols. Remarkably, calcined SiC is also active and promotes higher alcohol yields, possibly by activating CO_2 and subsequent formation of absorbed CH_x*. Best performance with a higher alcohol selectivity of 28.7% at a CO_2 conversion of 29.6%, together with good stability was obtained over an optimized K-0.82-FeIn/Ce-ZrO_2_900 (in the presence of SiC_900) catalyst. These results show that the addition of Fe, known to be effective for C-C coupling reactions in e.g. FT synthesis, to a state-of-the-art methanol synthesis catalyst for CO_2 (In_2O_3) allows the synthesis of higher alcohols by CO_2 hydrogenation. In addition, the co-production of considerable amounts of valuable olefins was observed, which will have a positive effect on the techno-economic potential of the reaction. This investigation also provides compelling evidence that activated SiC is catalytically active and as such could be a very interesting catalyst for CO_2 transformation reactions.

In **Chapter 5**, hydrotalcite-derived mono- and bimetallic CuNi-PMO catalysts were explored for the Guerbet coupling of ethanol to 1-butanol in a continuous flow set-up with times on stream up to 160 h. Catalyst performance was best for the bimetallic catalyst giving an ethanol conversion of 47.3% and a very promising space time yield of 1-butanol of 1.43 $g_{pro}\ g_{cat}^{-1}\ h^{-1}$ (320 °C, 7 MPa, LHSV=15 mL $g^{-1}\ h^{-1}$). When using the monometallic Ni-PMO catalyst, acetaldehyde was the main product, though only in limited amounts. Two regimes with different product distributions were observed for Cu-PMO and CuNi-PMO catalyst with time on stream, with acetaldehyde in the first regime, and 1-butanol as the main product in the second one. Experiments at different temperatures and pressures show that the transition from regime 1 to 2 occurs at shorter runtimes when using higher temperatures and pressures. Detailed characterization studies on spent CuNi-PMO catalysts at specific runtimes revealed that the change in chemo-selectivity from acetaldehyde to 1-butanol with runtime is mainly due to an increase of the basicity of the catalyst and neither to major changes in the type and size of metallic nanoparticles, nor to major changes in morphology.

In conclusion, this PhD thesis presented catalytic systems for higher alcohol synthesis from syngas conversion, CO_2 hydrogenation and Guerbet coupling of ethanol with remarkably improved performance in terms of activity, selectivity and stability in comparison with the

state-of-the-art performance as reported in the literature. Moreover, relations between catalyst structure and performance have been investigated based on detailed catalyst characterization studies and in depth analyses of products.